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1988 J. Phys. A: Math. Gen. 21 363

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## Some results in the exact self-consistent field theory of Brueckner

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Received 29 July 1987

**Abstract.** A particularly simple and transparent formulation of the exact self-consistent field theory of Brueckner is presented and a number of new results are proved. In particular, it is shown that the exact self-consistent function is one which among the functions in the trial space has maximum overlap with the exact eigenfunction and satisfies both the Brillouin and Brillouin-Brueckner properties and that the basic functional of the theory has optimal solutions other than the exact self-consistent function. The constraints under which the optimisation of the basic functional yields the desired solution are clearly stated and explained. Particularly simple proofs of some earlier results are given and some earlier results are strengthened.

### 1. Introduction

The exact self-consistent field (SCF) theory of Brueckner (Brueckner 1954, 1955a, b, Brueckner *et al* 1954, Brueckner and Levinson 1955) is called exact because though neither the Hamiltonian nor the wavefunction is exact, the energy (not the eigenvalue) is in fact exact. However, as is well known, it is not all that easy to determine exact energies and the exact SCF theory is purely theoretical: yet in slightly less exact forms it has practical applications. Furthermore, the study of the exact SCF theory is important because of the insight one gains about the reaction operator and methods developed by the theory have considerable relevance for the so-called *ab initio* calculations.

A simple, yet rigorous, account of the theory is presented here and a particularly simple proof of a very general version of the Brillouin theorem given by Sharma and SriRanganathan (1980) (see also Pian and Sharma 1981) is exploited to show that the Brillouin-Brueckner theorem and the Brillouin theorem are essentially the same result and the exact SCF wavefunction has both these properties. The basic functional of the exact SCF theory is investigated and the constraints are established under which the optimisation produces the exact SCF wavefunction and the corresponding eigenvalue. In particular it is shown that the functional has other optimal solutions if the constraints are not implemented.

The exact SCF theory is described here from first principles—all the operators of the theory are defined and simple proofs of all essential results are given. In order to keep the account simple, a treatment for only a non-degenerate eigenvalue of the Hamiltonian is given. The extension of the results to the degenerate case is relatively straightforward and uses few new concepts or results.

## 2. Formalities

All operators appear as bold letters except the zero operator which appears as a simple zero (0). The choice of a bold letter  $\mathbf{O}$  for a non-zero operator is unfortunate, but is retained for the sake of conformity with much of the earlier literature on the subject.

Let  $\mathbf{H}$  be the Hamiltonian of a many-electron system. Let  $\Psi$  be the exact eigenfunction of  $\mathbf{H}$  belonging to the isolated non-degenerate eigenvalue  $E$ . Let  $T$  be any trial space (a set of vectors whose members belong to a specified family such as the family of products of one-electron functions (Hartree type) or the family of single Slater determinants of one-electron functions (Hartree-Fock type)). Let  $\phi$  be a member of  $T$  with a non-zero overlap with  $\Psi$ . Let  $\mathbf{O}$  be the projection on the one-dimensional subspace of the Hilbert space  $H$  spanned by  $\phi$  and let  $\mathbf{P}$  be the projection on the orthogonal complement of this subspace, i.e.

$$\mathbf{OP} = \mathbf{PO} = 0 \quad (1)$$

$$\mathbf{O} + \mathbf{P} = \mathbf{I} \quad (2)$$

where  $\mathbf{I}$  is the identity operator on  $H$ . Next an operator  $\mathbf{H}'$  is defined for brevity and an operator  $\mathbf{K}$  is defined which is one of the fundamental operators in this theory:

$$\mathbf{H}' = \mathbf{H} - E\mathbf{I} \quad (3)$$

$$\mathbf{K} = \alpha\mathbf{O} - \mathbf{PH}'\mathbf{P} \quad (4)$$

where  $\alpha \neq 0$  is a real constant. The operator  $\mathbf{K}$  whose self-adjointness follows from theorem 2 in appendix A of Weinstein and Stenger (1972) is invertible if and only if the following conditions are satisfied.

(i)  $\phi$  and  $\Psi$  have non-zero overlap: this is because if  $\phi$  is perpendicular to  $\Psi$  then  $\Psi$  lies entirely in the image space of  $\mathbf{P}$  and therefore

$$\mathbf{K}\Psi = 0 \quad (5)$$

and a linear operator which takes any non-zero vector to zero cannot be inverted.

(ii)  $E$  is an isolated point eigenvalue; if it were not then it would be a limit point of the spectrum of  $\mathbf{H}$  (see Weyl 1909): at such points for infinitely many vectors  $\chi_i$ ,  $\mathbf{K}\chi_i$  is as close to zero as one likes which will imply that 0 is a point in the spectrum of  $\mathbf{K}$  and a self-adjoint operator which has 0 in its spectrum cannot be inverted.

(iii)  $\alpha$  is non-zero, because if  $\alpha$  were zero, then

$$\mathbf{K}\phi = 0 \quad (6)$$

and  $\mathbf{K}$  cannot be invertible for the same reason as in (i). A more sophisticated and complete proof for the case when  $E$  is degenerate with finite multiplicity is given in Wilson and Sharma (1981). All the properties which make  $\mathbf{K}$  invertible have been assumed in the definitions of  $\phi$ ,  $E$  and  $\alpha$  above, so hereafter  $\mathbf{K}$  will be regarded as invertible.

Let  $\mathbf{K}^{-1}$  be the inverse of  $\mathbf{K}$ , then

$$(\alpha\mathbf{O} - \mathbf{PH}'\mathbf{P})\mathbf{K}^{-1} = \mathbf{I} \quad (7)$$

from which we easily deduce with the help of (1) and the self-adjointness of  $\mathbf{O}$ ,  $\mathbf{K}$  and  $\mathbf{K}^{-1}$  that

$$\alpha\mathbf{OK}^{-1} = \mathbf{O} \quad (8)$$

$$\alpha\mathbf{K}^{-1}\mathbf{O} = \mathbf{O}. \quad (9)$$

In other words,  $\mathbf{K}^{-1}$  commutes with  $\mathbf{O}$ . Further

$$-\mathbf{PH}'\mathbf{PK}^{-1} = \mathbf{P} \quad (10)$$

$$\mathbf{OK}^{-1}\mathbf{P} = \mathbf{PK}^{-1}\mathbf{O} = 0 \quad (11)$$

and

$$-\mathbf{PH}'\mathbf{PK}^{-1}\mathbf{P} = \mathbf{P}. \quad (12)$$

Since  $\mathbf{K}^{-1}$  commutes with  $\mathbf{O}$ , one can write

$$\mathbf{K}^{-1} = \mathbf{OK}^{-1}\mathbf{O} + \mathbf{PK}^{-1}\mathbf{P} \quad (13)$$

or

$$\mathbf{PK}^{-1} = \mathbf{K}^{-1}\mathbf{P} = \mathbf{PK}^{-1}\mathbf{P} \quad (14)$$

and  $\mathbf{K}^{-1}$  commutes with  $\mathbf{P}$  also.

One abbreviates (14) by defining an operator  $\mathbf{T}$  by

$$\mathbf{T} = \mathbf{PK}^{-1} = \mathbf{K}^{-1}\mathbf{P} = \mathbf{PK}^{-1}\mathbf{P}. \quad (15)$$

It immediately follows that  $\mathbf{P}$  and  $\mathbf{T}$  commute and

$$\mathbf{PT} = \mathbf{TP} = \mathbf{T} \quad (16)$$

and hence

$$\mathbf{OT} = \mathbf{TO} = 0. \quad (17)$$

Equation (12) can now be abbreviated to

$$-\mathbf{PH}'\mathbf{T} = \mathbf{P} \quad (18)$$

and its adjoint is

$$-\mathbf{TH}'\mathbf{P} = \mathbf{P}. \quad (19)$$

It matters not what value of  $\alpha$  is taken in defining  $\mathbf{K}$  and therefore  $\mathbf{T}$ ;  $\mathbf{T}$  satisfies equation (18), which is its most basic property: indeed  $\mathbf{T}$  can be regarded as a solution of (18). Thus  $\mathbf{T}$  is independent of  $\alpha$  and Löwdin (1962) and others have written it as  $\mathbf{P}/(\mathbf{E} - \mathbf{H})$  rather than as  $\mathbf{PK}^{-1}\mathbf{P}$ . It is shown by Wilson and Sharma (1982) that such a notation can lead first to confusion and thence to disaster. One useful property of  $\mathbf{T}$  is expressed in the equation

$$\mathbf{T} = \mathbf{K}^{-1} - \alpha^{-1}\mathbf{O} \quad (20)$$

which is easily deduced with the help of equations (2), (8) and (15).

With the help of  $\mathbf{T}$  an operator  $\mathbf{\Omega}$  is now defined

$$\mathbf{\Omega} = \mathbf{I} + \mathbf{TH}' = \mathbf{I} + \mathbf{PK}^{-1}\mathbf{PH}' \quad (21)$$

which on multiplying on the right by  $\mathbf{P}$  and using (19) immediately gives

$$\mathbf{\Omega}\mathbf{P} = \mathbf{P} + \mathbf{TH}'\mathbf{P} = \mathbf{P} - \mathbf{P} = 0 \quad (22)$$

and consequently

$$\mathbf{\Omega} = \mathbf{\Omega}\mathbf{O} + \mathbf{\Omega}\mathbf{P} = \mathbf{\Omega}\mathbf{O}. \quad (23)$$

On the other hand from (21) and (23)

$$\mathbf{\Omega} = \mathbf{\Omega}\mathbf{O} = \mathbf{O} + \mathbf{TH}'\mathbf{O} = \mathbf{O} + \mathbf{THO} - \mathbf{ETO} = \mathbf{O} + \mathbf{THO}. \quad (24)$$

Hence

$$\mathbf{O}\Omega = \mathbf{O} \quad (25)$$

and

$$\mathbf{P}\Omega = \Omega - \mathbf{O}\Omega = \Omega - \mathbf{O}. \quad (26)$$

Remembering that  $\Psi$  is an eigenvector of  $\mathbf{H}$  belonging to the eigenvalue  $E$ , i.e.

$$\mathbf{H}'\Psi = 0 \quad (27)$$

it follows from (21) that

$$\Omega\Psi = \Psi \quad (28)$$

and

$$\mathbf{H}\Omega\Psi = \mathbf{H}\Psi = E\Psi = E\Omega\Psi \quad (29)$$

or

$$\mathbf{H}'\Omega\Psi = 0. \quad (30)$$

Since

$$\mathbf{O}\Psi = \beta\phi \quad (31)$$

for some complex number,  $\beta$ , it follows from (30) and (23) that

$$\mathbf{H}'\Omega\phi = 0. \quad (32)$$

Any vector  $\chi$  can be written as

$$\chi = \mathbf{O}\chi + \mathbf{P}\chi = c\phi + \mathbf{P}\chi \quad (33)$$

for some complex number  $c$ , it follows from (22) and (33) that

$$\mathbf{H}'\Omega\chi = c\mathbf{H}'\phi + \mathbf{H}'\Omega\mathbf{P}\chi = 0 \quad (34)$$

which proves that

$$0 = \mathbf{H}'\Omega = \mathbf{H}' + \mathbf{H}'\mathbf{T}\mathbf{H}' = \mathbf{H} + \mathbf{H}\mathbf{T}\mathbf{H} - \mathbf{E}\mathbf{I} - \mathbf{E}\mathbf{T}\mathbf{H} - \mathbf{E}\mathbf{H}\mathbf{T} + \mathbf{E}^2\mathbf{T}. \quad (35)$$

Multiplying (35) by  $\mathbf{O}$  both on the left and the right and using (17) gives

$$\mathbf{O}\mathbf{E}\mathbf{O} = \mathbf{O}(\mathbf{H} + \mathbf{H}\mathbf{T}\mathbf{H})\mathbf{O}. \quad (36)$$

Since  $\Omega$  itself is not zero (for if it were it would imply from its definition (21) that  $-\mathbf{T}$  was inverse of  $\mathbf{H}'$ , but  $\mathbf{H}'$  is not invertible because it takes  $\Psi$  to zero) it follows after taking into account (22) that  $\Omega$  is effectively non-zero only on the one-dimensional subspace  $\mathbf{O}(H)$ . In other words, for the vector  $\phi$  which spans the image space of  $\mathbf{O}$

$$\Omega\phi \neq 0 \quad (37)$$

then

$$\mathbf{H}'\Omega\phi = 0 \quad (38)$$

implies that  $\Omega\phi$  is an eigenvector of  $\mathbf{H}$  belonging to the eigenvalue  $E$ , and since  $E$  has been assumed to be non-degenerate this means that

$$\Omega\phi = s\Psi \quad (39)$$

for some complex number  $s$ . The modulus of  $s$  shall be determined presently. To this end it is assumed that the eigenvector  $\Psi$  is normalised to unity:

$$\langle \Psi | \Psi \rangle = 1. \tag{40}$$

Note that the normalisation of  $\Psi$  used here is different from that used in earlier works (e.g., Löwdin 1962, Wilson and Sharma 1982). Taking the inner product of (39) by  $s\Psi$  gives

$$|s|^2 = \langle s\Psi | s\Psi \rangle = 1 + \langle \mathbf{TH}'\phi | \mathbf{TH}'\phi \rangle = 1 + \langle \mathbf{TH}\phi | \mathbf{TH}\phi \rangle = 1 + \langle \phi | \mathbf{HT}^2\mathbf{H} | \phi \rangle \tag{41}$$

and thence

$$|\langle \phi | \Psi \rangle| = |\langle \phi | \Omega | \phi \rangle| / |s| = |1 + \langle \phi | \mathbf{TH}'\phi \rangle| / |s| = 1 / |s| \tag{42}$$

with  $|s|$  given by (41).

In the trial space  $T$  one wishes to find a  $\phi$  such that its overlap with  $\Psi$ , that is  $|\langle \phi | \Psi \rangle|$ , is maximum. The exact SCF theory does not actually find such a  $\phi$ , but tells one what some of the properties of such a  $\phi$  are.

Before concluding this section, it ought to be pointed out that one consequence of (39) is that whenever  $\chi$  is a vector such that

$$\mathbf{O}\chi \neq 0 \tag{43}$$

then  $\mathbf{O}\chi$  is some linear multiple of  $\Psi$  and therefore an eigenvector of  $\mathbf{H}$  belonging to the eigenvalue  $E$ .

### 3. The exact SCF theory

It is commonly stated in previous works that the exact SCF wavefunction is the function corresponding to the optimal value of the functional  $\langle \Phi | \mathbf{H} + \mathbf{HT}_\phi \mathbf{H} | \Phi \rangle$  in the trial space with unit  $\Phi$ ; here  $\phi$  as a subscript of  $\mathbf{T}$  implies that the resolution of identity (2) is made with the help of the operator  $\mathbf{O}$  which is the projection on the span of the vector  $\phi$  which corresponds to the optimal value of the functional. However, since the value of  $\langle \phi | \mathbf{H} + \mathbf{HT}_\phi \mathbf{H} | \phi \rangle$  is a constant (actually the eigenvalue  $E$ ), the functional is optimal everywhere in the trial space.

The work which follows will show that the exact SCF wavefunction has the following properties: consider the functional  $\langle \Phi | \mathbf{H} + \mathbf{HTH} | \Phi \rangle$  for unit  $\Phi$  with a fixed  $\mathbf{T}$  defined with the help of some fixed vector  $\phi_r$  belonging to the trial space  $T$ , then the function  $\Phi_o$  corresponding to the optimal value of the functional will, in general, be different from  $\phi_r$ . However, there is a choice of  $\phi_r$  for which

$$\Phi_o = \phi_r \tag{44}$$

and this is precisely the exact SCF wavefunction which is not exact but is the function in the trial space with maximal overlap with the exact eigenfunction  $\Psi$ .

Consider first the functional  $\langle \Phi | \mathbf{H} + \mathbf{HTH} | \Phi \rangle$  for normalised  $\Phi$  without restricting either  $\Phi$  or the fixed vector  $\phi_r$  whose span defines the projection  $\mathbf{O}$  in (2) to the trial space  $T$ . Then the optimal solution satisfies

$$(\mathbf{H} + \mathbf{HTH})\Phi_o = \mu \Phi_o. \tag{45}$$

Now

$$\mathbf{H} + \mathbf{HTH} = \mathbf{H}(\mathbf{I} + \mathbf{TH}) = \mathbf{H}\Omega + \mathbf{EHT} = \mathbf{H}\Omega + \mathbf{EH}'\mathbf{T} + \mathbf{E}^2\mathbf{T} = \mathbf{E}\Omega + \mathbf{EH}'\mathbf{T} + \mathbf{E}^2\mathbf{T}. \tag{46}$$

Multiplying (46) by  $\mathbf{O}$  on the left gives

$$E(\mathbf{O}\mathbf{\Omega} + \mathbf{O}\mathbf{H}'\mathbf{T})\Phi_o = \mu\mathbf{O}\Phi_o \quad (47)$$

which, in view of (25), can be written as

$$E(\mathbf{O}(\mathbf{I} + \mathbf{H}'\mathbf{T}))\Phi_o = \mu\mathbf{O}\Phi_o \quad (48)$$

and can be further reduced to

$$E\mathbf{\Omega}^*\Phi_o = \mu\mathbf{O}\Phi_o \quad (49)$$

with the help of the adjoint of (21).

Let

$$\mathbf{O}\Phi_o = t\phi_f \quad (50)$$

and

$$\mathbf{\Omega}\phi_f = s\Psi. \quad (51)$$

Taking the inner product of (49) with  $\Phi_o$  gives

$$Es^*t^*\langle\Psi|\Phi_o\rangle = \mu\langle\Phi_o|\mathbf{O}|\Phi_o\rangle = \mu|t|^2. \quad (52)$$

Multiplying (45) on the left by  $\mathbf{P}$  gives

$$E(\mathbf{P}\mathbf{\Omega} + \mathbf{P}\mathbf{H}'\mathbf{T} + \mathbf{E}\mathbf{T})\Phi_o = \mu\mathbf{P}\Phi_o \quad (53)$$

which, in view of (26) and (18), can be rewritten as

$$E[(\mathbf{\Omega} - \mathbf{O} - \mathbf{P}) + \mathbf{E}\mathbf{T}]\Phi_o = \mu\mathbf{P}\Phi_o \quad (54)$$

and reduces further with the help of (2) and (21) to

$$E(\mathbf{T}\mathbf{H}' + \mathbf{E}\mathbf{T})\Phi_o = \mu\mathbf{P}\Phi_o \quad (55)$$

and finally with the help of (3), (55) takes the simple form

$$E\mathbf{T}\mathbf{H}\Phi_o = \mu\mathbf{P}\Phi_o. \quad (56)$$

Thus the optimal solution  $\Phi_o$  for a fixed  $\mathbf{T}$  corresponding to  $\mathbf{O}$  defined as the projection on the one-dimensional subspace spanned by an arbitrary  $\phi_f$  in the Hilbert space satisfies (49) and (56) to which it does not seem easy to give any significant physical interpretation. However, if  $\phi_f$  is chosen in such a way that the optimal solution  $\Phi_o$  satisfies

$$\Phi_o = \phi_f \quad (57)$$

or, in other words, if

$$\mathbf{P}\Phi_o = 0 \quad (58)$$

then

$$\mathbf{T}\mathbf{H}\Phi_o = \mathbf{T}\mathbf{H}\phi_f = 0. \quad (59)$$

In that case  $t$  of equation (50) is 1 and it follows from (41) that

$$|s|^2 = 1 \quad (60)$$

and  $s$  can be taken to be 1 by a suitable choice of phase of  $\phi_r$ . Further, it follows from (36) that

$$\mu = E \quad (61)$$

and (52) reduces to

$$\langle \Psi | \Phi_0 \rangle = 1 \quad (62)$$

which is possible for unit vectors  $\Psi$  and  $\Phi_0$ , if and only if

$$\Psi = \Phi_0.$$

Thus the optimal solution with the property that the optimal functional is the function whose span is the image space of  $\mathbf{O}$  in the definition of  $\mathbf{T}$  is the exact eigenfunction provided the trial space is the whole Hilbert space. When one restricts oneself to the trial space  $T$  which is not the whole Hilbert space, then equations (59) and (60) are only approximately satisfied even though

$$\mathbf{P}\Phi_0 = 0 \quad (63)$$

$\mathbf{TH}\Phi_0$  is no longer zero, but hopefully small.

It will now be shown that provided the trial space  $T$  is of either Hartree or Hartree-Fock type then  $\mathbf{TH}\Phi_0$  is small enough to guarantee that the overlap between  $\Phi_0$  and  $\Psi$  is maximum. To prove this it seems necessary to follow a completely different line of reasoning.

Suppose that  $\Phi_0$  is the optimal solution of  $\langle \Phi | \mathbf{H} + \mathbf{HTH} | \Phi \rangle$  for unit  $\Phi$  when  $T$  is defined with the help of the projection  $\mathbf{O}$  on the one-dimensional subspace spanned by  $\Phi_0$ , the trial space  $T$  being of either Hartree or Hartree-Fock type. Let  $\Phi_{se}$  be singly excited relative to  $\Phi_0$ , in other words,  $\Phi_{se}$  belongs to  $T$  and so does any linear combination of  $\Phi_0$  and  $\Phi_{se}$  and further

$$\langle \Phi_{se} | \Phi_0 \rangle = 0. \quad (64)$$

Thus it satisfies all the conditions of the Brillouin theorem as stated by Sharma and SriRanganathan (1980); therefore

$$\langle \Phi_{se} | \mathbf{H} + \mathbf{HTH} | \Phi_0 \rangle = 0 \quad (65)$$

which, in view of (17) and (3) can be written as

$$\langle \Phi_{se} | \mathbf{H}(\mathbf{I} + \mathbf{TH}') | \Phi_0 \rangle = 0 \quad (66)$$

and which reduces further, with the help of (21), (39) and (27) to

$$\langle \Phi_{se} | \Psi \rangle = 0. \quad (67)$$

Thus all functions which are singly excited relative to  $\Phi_0$  are orthogonal to the exact wavefunction  $\Psi$ , which is precisely the condition that  $\Phi_0$  corresponds to the maximum of  $|\langle \Phi_0 | \Psi \rangle|$  in  $T$ . The ease with which (67) has been established in this formulation should be noted—this result, or rather something which is equivalent to it and which will be established in the next section, has been described as the Brillouin-Brueckner theorem by Löwdin (1962); it really is only a simple example of the Brillouin theorem as stated by Sharma and SriRanganathan (1980).

The optimal solution  $\Phi_0$  no longer satisfies (45) because optimisation is now constrained to the trial space  $T$ , but it does satisfy

$$\mathbf{H}_b\Phi_0 = E_b\Phi_0 \quad (68)$$



where  $H_b$  corresponds to  $H + HTH$  in the same way as the Hartree-Fock Hamiltonian  $H_{HF}$  corresponds to  $H$  and  $E_b$  is the eigenvalue whose relation to the exact energy eigenvalue  $E$  will soon be determined.

The Brueckner potential  $V_b$  is defined by

$$V_b = H - H_b \quad (69)$$

and in view of (67) it follows immediately from the first-order perturbation theory that

$$\langle \Phi_{se} | V_b | \Phi_o \rangle = 0 \quad (70)$$

and since  $\Phi_o$  is an eigenvector of  $H_b$  and  $\Phi_{se}$  is orthogonal to  $\Phi_o$ , it follows also that

$$\langle \Phi_{se} | H | \Phi_o \rangle = 0 \quad (71)$$

which, in this particular case, ought to be described as the Brillouin property and is a direct consequence of the Brillouin theorem.

Before proceeding further it is interesting to note that the functional  $\langle \Phi | H + HTH | \Phi \rangle$  for unit  $\Phi$  and  $T$  defined with the help of projection  $O$  on the span of the optimal solution  $\Phi_o$ , has other optimal solutions as well. To see this clearly, take the whole Hilbert space as the trial space, then

$$\Phi_o = \Psi. \quad (72)$$

The other optimal solutions  $\Xi$  are eigenvectors of  $H + HTH$  perpendicular to  $\Psi$  and therefore satisfy

$$P\Xi = \Xi \quad (73)$$

and therefore, from (56)

$$ETH\Xi = \mu\Xi. \quad (74)$$

Using (20) and operating on the left by  $K$  gives

$$EK(K^{-1} - \alpha^{-1}O)\Xi = \mu K\Xi. \quad (75)$$

Remembering that (72) implies

$$O\Xi = 0 \quad (76)$$

(75) reduces to

$$K\Xi = (E/\mu)\Xi. \quad (77)$$

Thus these optimal solutions are eigenvectors of  $K$  perpendicular to  $\Psi$ , which are clearly also eigenvectors of  $H$  perpendicular to  $\Psi$ . Thus the other optimal solutions are simply the excited states. When one restricts oneself to the trial space  $T$ ,  $O$  is the projection on the span of  $\Phi_o$ , and then optimal solutions in the image space of  $P$  are merely approximations to the excited states.

#### 4. Some other properties in the SCF theory

With the help of (69) one writes

$$\begin{aligned} H + HTH &= H_b + V_b + (H_b + V_b)T(H_b + V_b) \\ &= H_b + H_bTH_b + H_bTV_b + V_bTH_b + V_b + V_bTV_b \end{aligned} \quad (78)$$

and then one has with the help of (68) and (17)

$$\langle \Phi_o | \mathbf{H} + \mathbf{H}\mathbf{T}\mathbf{H} | \Phi_o \rangle = \langle \Phi_o | \mathbf{H}_b + \mathbf{V}_b + \mathbf{V}_b \mathbf{T} \mathbf{V}_b | \Phi_o \rangle. \quad (79)$$

Next one defines the reaction operator  $\mathbf{t}$  by

$$\mathbf{t} = \mathbf{V}_b + \mathbf{V}_b \mathbf{T} \mathbf{V}_b \quad (80)$$

and (79) then reduces to

$$E = \langle \Phi_o | \mathbf{H} + \mathbf{H}\mathbf{T}\mathbf{H} | \Phi_o \rangle = E_b + \langle \Phi_o | \mathbf{t} | \Phi_o \rangle. \quad (81)$$

Since each  $\Phi_{se}$  is perpendicular to  $\Psi$ , if one takes the closure  $S$  of the span of all the singly excited states (note that linear combinations of singly excited states need not be singly excited: both 1s3s and 2s4s are singly excited relative to 1s2s but their linear combination no longer belongs to the trial space and one will have to stretch one's definition of singly excited states in order to regard the aforementioned linear combination as a singly excited state) then this subspace  $S$  is perpendicular to  $\Psi$  and does not play any part as far as deducing the properties of  $\Psi$  is concerned. Therefore, one can regard  $S^\perp$  as the whole space. Let  $P_1$  be the projection on  $S$ , then define projection  $Q$  by

$$Q = P - P_1 \quad (82)$$

and

$$P_1 Q = Q P_1 \quad (83)$$

in other words,  $Q$  is the projection on the orthogonal complement of  $S$  in the image space of  $P$ . In  $S^\perp$

$$\hat{I} = O + Q \quad (84)$$

where  $\hat{I}$  is the identity operator on  $S^\perp$ . Regarding  $S^\perp$  as the whole space, one can now define  $\hat{T}$  and  $\hat{\Omega}$  corresponding to  $T$  and  $\Omega$  on the whole space:

$$\hat{T} = Q[\alpha O - Q(\mathbf{H} - E)Q]^{-1} Q \quad (85)$$

and

$$\hat{\Omega} = O + Q\hat{T}QH O \quad (86)$$

and since  $H_b$  commutes with  $O$ , one can write

$$\hat{\Omega} = O + Q\hat{T}QV_b O = O + \hat{T}QV_b O. \quad (87)$$

$\Omega$  defined on the whole space commutes with  $P_1$ , because (22), i.e.

$$\Omega P = 0 \quad (88)$$

implies

$$\Omega P_1 = 0 \quad (89)$$

and (64) implies that

$$P_1 \Psi = 0 \quad (90)$$

which in turn implies that

$$P_1 \Omega = 0. \quad (91)$$

This means that  $\Omega$  agrees with  $\hat{\Omega}$  in  $S^\perp$  and in  $S$  it is zero. Therefore, one can drop the hat from  $\hat{\Omega}$  in (87) and regard it as an operator on the whole Hilbert space. This proof which is absolutely complete and rigorous should be compared with that given by Löwdin (1962) where a large number of difficult steps are omitted.

Equation (91) implies that

$$P_1 TH'O = P_1 THO = 0 \quad (92)$$

which in view of (69) implies that

$$P_1 TV_b O + P_1 TH_b O = 0. \quad (93)$$

On the other hand since  $O$  is a projection on an eigenspace of  $H_b$  implies that  $H_b$  commutes with  $O$ , i.e.

$$H_b O = O H_b. \quad (94)$$

With the help of equations (94) and (17), (93) reduces to

$$P_1 TV_b O = 0. \quad (95)$$

The main conclusion (65) from the Brillouin theorem, after taking into account (17), (68), (78), (80) and (95), takes the form

$$\langle \Phi_{se} | T | \Phi_o \rangle = 0. \quad (96)$$

This is the alternative form of the so-called Brillouin-Brueckner theorem which was referred to in the previous section. In Löwdin (1962), (96) is deduced first and (68) is found to be a consequence of that: in this work (68) is proved first as a particular case of the Brillouin theorem and (96) is easily deduced from that. All the results established in this work have remarkably simple proofs and it is hoped that simple proofs give a deeper understanding of the subject.

## 5. Concluding remarks

It should be emphasised that in all the applications the Hartree-type functions are more commonly used in the Brueckner theory and such applications have been particularly successful in dealing with nuclear matter. Independent particle models based on the theory have been successfully applied to numerous problems concerning many-electron systems, such as for studying the electronic clouds in atoms, the mobile  $\pi$  electrons in the Hückel scheme and the band theory of solids: references to these applications will be found in Löwdin (1962). Methods based on the theory are also used in *ab initio* and semiempirical calculations of atomic and molecular properties. It is hoped that the insight gained by the simplifications achieved and new results proved in this work will make the Brueckner theory even more useful than it currently is.

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